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Ultrasmall semiconducting polymer quantum boxes having three-dimensional confinement volumes of 1-2 nm^3 are prepared by self-organization of blends of an ABA block conjugated copolymer with its component homopolymer A. Optical experiments evidence quantum confinement effects on excitons in the novel low dimensional semiconductors, including observation of new discrete optical transitions in photoluminescence excitation spectra at room temperature, enhanced luminescence, and exceptional temperature and electric field stability of the quasi zero-dimensional excitons. These results provide the first evidence of quantum confinement effects in semiconducting polymers and a general approach to preparing organic semiconductor quantum boxes which have potential applications in molecular and conventional optoelectronic and photonic devices.

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Self-Assembled Semiconducting Polymer Quantum Boxes

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Abstract

Ultrasmall semiconducting polymer quantum boxes having three-dimensional confinement volumes of 1-2 nm^3 are prepared by self-organization of blends of an ABA block conjugated copolymer with its component homopolymer A. Optical experiments evidence quantum confinement effects on excitons in the novel low dimensional semiconductors, including observation of new discrete optical transitions in photoluminescence excitation spectra at room temperature, enhanced luminescence, and exceptional temperature and electric field stability of the quasi zero-dimensional excitons. These results provide the first evidence of quantum confinement effects in semiconducting polymers and a general approach to preparing organic semiconductor quantum boxes which have potential applications in molecular and conventional optoelectronic and photonic devices.

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Low dimensional inorganic semiconductor systems have been of much scientific and technological interest in the past 25 years (1-6). Compared to bulk semiconductors, low dimensional semiconductors exhibit novel or modified electronic and optical properties due to spatial confinement of charge carriers or excitons (1-6). Increased exciton binding energy, enhanced oscillator strengths, large Stark shifts, and enhanced optical nonlinearities in low dimensional semiconductors have led to device applications such as diode lasers, Stark effect optical modulators, self-electrooptic effect devices, optical waveguide switches, and cavity-less nonlinear optical bistability (3-6). Organic semiconductors with reduced dimensionality are also of growing interest owing to their expected unique features compared to the corresponding inorganic semiconductors (7-13). Defect-free heterostructures can be more readily fabricated due to the weak Van der Waals interactions between organic molecules. The smaller dielectric constant of organic molecules and polymers [~3-4] compared to inorganic semiconductors [≥ 10] could result in strong Coulomb interaction between electrons and holes, leading to strong excitonic effects and large exciton binding energies [~0.5-1.0 eV]. Improved electric field stability of excitons in organic quantum-well structures has also been suggested from theoretical studies (10).

To achieve quantum confinement effects in a semiconductor heterostructure requires that the size of the potential well structure be comparable or smaller than the charge carrier or exciton Bohr radius in at least one spatial direction (1,5,6). Exciton Bohr radii (a_B) in bulk organic semiconductors are generally small, ca. 10-15 Å, for example: 12-13 Å in 3,4,9,10-perylenetetracarboxylic dianhydride(7); 10-12 Å in various single crystal polydiacetylenes (14); 13 Å in poly(benzobisthiazole-1,4-phenylene)(15). This size requirement places a severe limitation on the

possible methods that could be used to prepare low dimensional organic semiconductor systems. To date, two conceptual approaches to the preparation of organic semiconductor quantum structures have been explored: (i) ultrahigh vacuum organic molecular beam deposition (OMBD) of layered heterostructures from small molecules(7,8); and (ii) heterostructured semiconducting polymers via block copolymerization(9-13,16). Layered nanostructures of naphthalene and perylene derivatives grown by OMBD have been shown to exhibit the characteristics of multiple quantum wells (MQWs) with one-dimensional exciton confinement (7). The two-dimensional excitons in such OMBD grown crystalline MQWs have been shown to be spatially extended (Wannier-like), almost spherical with Bohr radii of 1.3 nm, and to have binding energies as large as 150 meV which are larger than in inorganic MQWs by an order of magnitude (7). Although there have been many theoretical calculations predicting quantum confinement effects in block conjugated copolymer chains (9-11), this approach has so far not resulted in experimental realization (12,13,16) of quantum confined nanostructures in semiconducting polymers. The prior synthetic difficulty of preparing well-defined block conjugated copolymer heterostructures in which to test theoretical predictions was recently overcomed by the synthesis of a soluble and processible ABA triblock copolymer in our laboratory (16). However, our extensive studies of the block conjugated copolymer heterostructures did not reveal any evidence of the predicted quantum confinement effects (16).

We report here a novel approach to preparing quasi zero-dimensional (0-D) organic semiconductor systems and experimental observation of the associated quantum confinement effects. The approach exploits the self-organization of blends of an ABA copolymer with its component homopolymer A to prepare isolated boxes of the middle block B with uniform rectangular cross-sectional area of a single molecular chain. As many theoretical studies have suggested (9,10), an

$A_nB_mA_n$ block conjugated copolymer chain constructed from two different semiconducting polymers A_n and B_m with optical band gaps E_g^A and E_g^B, respectively, where $E_g^A > E_g^B$, represents a quantum-well structure with electron potential barrier of $\Delta E_g = E_g^A - E_g^B$. Thin films of such a triblock copolymer with an average composition $A_{20}B_9A_{20}$ (TBA-1, Fig.1a) where A and B are the repeat units of poly(benzobisthiazole-1,4-phenylene) (PBZT) and poly(2,5-benzoxazole) (2,5-PBO), respectively, were shown to be microphase separated (16), resulting in ordered aggregation of block copolymer chains (Fig.1b). The sizes of the PBZT microdomains in the microphase separated block copolymer can be expected to significantly exceed the bulk exciton Bohr radius of PBZT ($a_B = 13$ Å) and hence the absence of any quantum confinement effects (16). To overcome microphase separation, we propose that self-organization of suitable mixtures of a triblock copolymer with its component homopolymer 2,5-PBO will result in heterostructures in which three-dimensionally confined PBZT quantum boxes are well defined with ΔE_g of 0.81eV (Fig.1c). From the X-ray data for the homopolymers (17), such PBZT quantum boxes (Fig.1c) have the precise cross-sectional area of (0.35 x 0.58) nm^2 and a length l_m which varies with the number of PBZT repeat units incorporated into the B_m block. For TBA-1 the average l_m is 11 nm; for another triblock TBA-3 with composition $A_{25}B_4A_{25}$, $l_m = 5$ nm. The cross-sectional area of 0.203 nm^2 is a factor of 8.3 smaller than a_B^2 which implies very strong exciton confinement in two spatial directions; furthermore, the 3-D confinement volumes of the PBZT boxes in isolated TBA-1 and TBA-3 chains are 1.01-2.33 nm^3 compared to $a_B^3 = 2.20$ nm^3. Thus, in principle, the proposed approach can produce heterostructures suitable for investigating quantum confinement phenomena.

Blends of various compositions of TBA-1/2,5-PBO and TBA-3/2,5-PBO were prepared in nitromethane/GaCl$_3$ solution and thin films were prepared by spin coating onto silica or indium-tin-

oxide (ITO) coated substrates, using methods previously described for the pure copolymers and homopolymers (16,18). The detailed synthesis and characterization of the polymers and copolymers of Figure 1 have been reported (16). Additional experimental details, including the instruments and detailed methods used in our optical and photophysical experiments can be found elsewhere (19).

Optical absorption spectra of thin films of the block copolymer/homopolymer blend system (TBA-1/2,5-PBO) at room temperature (298K) showed absorption bands characteristic of the two components and the composition (Fig.2). The vibrationally resolved absorption band in the 420-500 nm region with maxima at 440 and 470 nm is due to the PBZT block and that in the range of 240-380 nm with maxima at 270, 344, and 360 nm is due to the 2,5-PBO chromophore. The sharp peaks at 470 nm(2.64 eV) and 360 nm (3.44 eV) are the excitonic energies of the PBZT and 2,5-PBO blocks, respectively, giving a potential well barrier ΔE_g of 0.81 eV in the heterostructures of Fig.1. No new optical transition or peak shift is detected in any of the TBA-1/2,5-PBO blends, even at 0.5% where the 1 triblock chain per 29 2,5-PBO chains ensures complete 3-D confinement of PBZT quantum boxes. These results indicate that optical absorption spectroscopy is not a sensitive probe of quantum confinement phenomena in these self-organized organic semiconductor systems.

Photoluminescence (PL) spectroscopy at 298K was more sensitive in revealing evidence of progressive spatial confinement in going from the pure triblock to blends containing 1 triblock chain per 1-29 2,5-PBO chains. The PL emission spectra of thin films of TBA-1 and TBA-1/2,5-PBO blends excited at 340 nm are shown in Fig.3a. Also shown for comparison is the emission spectrum of the PBZT homopolymer excited at 440 nm. It has previously been established that the broad and featureless PL spectrum of PBZT centered at 563 nm (Fig. 3a) originates from interchain excimer emission (20). The PL spectrum of the pure TBA-1 is also broad, nearly featureless, blue shifted

from that of pure PBZT, and can be similarly interpreted as originating from excimer emission from the microphase separated PBZT block. Progressive dispersion of TBA-1 in 2,5-PBO matrix in the blends from 15 to 3 mol% results in band narrowing and slight blue shift of a more structured band compared to the pure TBA-1 (Fig. 3a). The band narrowing as measured by the full-width-at-half-maximum (FWHM) dropped from 561 meV for 15% to 291 meV for the 3% blend. No further band narrowing was observed upon dilution from 3 to 0.5%. The corresponding Stokes shift of the PL peak (Fig. 3a) from the lowest energy absorption maximum (Fig.2) dropped from 455 and 224 meV for PBZT and TBA-1, respectively, to only 11 meV in the 0.5% blend. The negligible Stokes shift in the dilute blends indicates that the photogenerated excitons are confined to the lowest excited state. The small emission band at 380-430 nm is from the 2,5-PBO matrix. For all the blends, no variation of the PL spectra was observed upon varying the excitation wavelength from 320 nm to 440 nm. This means that even the preferential excitation of the 2,5-PBO matrix in the 320-380 nm region (Fig.2) results in efficient energy transfer to the spatially confined PBZT quantum boxes which act as exciton traps and radiative recombination centers.

Spatial confinement effects in semiconducting polymers observed as spectra changes in the PL emission of triblock/homopolymer blends (Fig. 3a) were also accompanied by large increases in photoluminescence quantum efficiency (Fig. 3b). To facilitate comparison of the relative PL quantum efficiency, all the TBA-1/2,5-PBO blend samples were excited at 435 nm. Variation of the PBZT block concentration from 18.4% in TBA-1 to a 1.5% blend results in more than a factor of three enhancement of the PL quantum yield (Fig. 3b). This enhancement of luminescence in the blends could be a result of decrease in the nonradiative recombination rate or increase in the radiative recombination rate, or both. Our additional observations from time-resolved (ps) PL decay dynamics

(19) of the same TBA-1/2,5-PBO blend system show that the exciton lifetime increases with decreasing concentration of the PBZT quantum boxes. Thus, decrease of the nonradiative recombination rate with increasing 3-D confinement of the quantum boxes is the likely origin of the observed luminescence enhancement. The contribution of bimolecular (interchain) quenching mechanism to the nonradiative recombination rate can be expected to decrease or terminate with increasing distance between PBZT blocks.

Photoluminescence excitation (PLE) spectroscopy has been widely used as one of the most sensitive probes of the discrete exciton states in low dimensional inorganic semiconductor systems (3). We have also found this to be the case in our self-organized semiconducting polymer quantum boxes. The room temperature (298K) PLE spectra of thin films of TBA-1 and several TBA-1/2,5-PBO blends corresponding to the PL spectra of Fig. 3a are shown in Fig. 4. These PLE spectra were obtained by monitoring the emission at 600 nm where there is negligible emission from the 2,5-PBO chromophore. The PLE spectra of TBA-1 and blends have features similar to the absorption spectra of Fig.2 as well as major differences. The presence of a large 340-360 nm band due to 2,5-PBO absorption shows that the 600-nm emission from the PBZT block contains a significant contribution from excitation energy transfer from 2,5-PBO. The PLE spectrum of TBA-1 (Fig.4) is similar to its absorption spectrum (Fig.2). However, a 10% blend which contains 1:1 TBA-1: 2,5-PBO ratio contains an entirely new band centered at 544 nm (2.28 eV) in the PLE spectrum. Further dilution of the PBZT block concentration in the blends, hence improved quantum box confinement, reveals clear peaks at 505 (2.46 eV) and 544 nm in the PLE spectra. In blends of 0.5-1.0%, additional new discrete peaks appear in the PLE spectra at 311 nm (3.99eV), 325 nm (3.82 eV), 392 nm (3.16 eV) and 422 nm (2.94 eV) (Fig.4). Similar results were observed in TBA-3/2,5-PBO blend system. This

observation of several new optical transitions in the PLE spectra of PBZT quantum boxes provides the first direct evidence of quantum confined exciton states in an organic semiconductor system.

The new optical transitions that are higher in energy compared to the optical gap of PBZT homopolymer (Fig.4) are qualitatively in accord with theoretical predictions for isolated block conjugated copolymer chains (9,10). These transitions originate from split-off electronic states upon quantum confinement and are similar in nature to commonly observed "miniband" states in low dimensional inorganic semiconductors. In contrast, the new optical transitions at 505 and 544 nm which are below the optical band gap of the lowest energy component have not been anticipated in prior theoretical studies. We propose that these below-gap excitonic states arise from spatial confinement induced delocalization of excitons along the length of the quantum boxes (0.35 x 0.58 x l_m nm^3, l_m = 5-11 nm) which is many times larger than the bulk exciton Bohr radius of PBZT (1.3 nm). A net effect of such an exciton delocalization could be the formation of below-gap states much like the well-known photogenerated bipolaron/polaron states in conjugated homopolymers (21).

The direct observation of the discrete optical transitions of excitons confined in semiconducting polymer quantum boxes at room temperature (Fig. 4) suggests that the binding energy of the excitons must be large. Additional evidence of the remarkable stability of these quasi 0-D excitons was found in the results of low temperature (77K) PL studies (Fig. 5a, 5b) and electric field-induced PL quenching experiments at 298K (Fig. 5c). Comparison of the PL spectra at 77 and 298K for a 15% blend, where there is poor confinement of the PBZT quantum boxes, shows a red shift and PL intensity redistribution at 77K (Fig. 5a). This arises from the longer exciton lifetime at 77K which facilitates exciton migration or relaxation to the lowest excited state. However, in a 0.5% blend, where there is complete confinement of the PBZT quantum boxes, the PL spectra at 77 and

298K are nearly identical (Fig. 5b), indicating that the electrons and holes of the excitons are confined to the lowest energy quantum box states. Large electric field-induced PL quenching of up to 10-55% at 10^6V/cm was observed in the triblock, homopolymers, and some blends (>3%) (Fig. 5c) in accord with similar observations on conjugated polymers by others (22). In contrast, field-induced PL quenching was not observed in the 0.5-3.0% blends at electric fields of up to 2.0 x 10^6 V/cm. This exceptional electric field stability of excitons in PBZT quantum boxes reflects their strong 3-D confinement and large binding energy. The extent of electric field-induced dissociation of excitons as detected by PL quenching under external electric field depends on the binding energy of the excitons (22) and presumably also on the confinement dimensionality.

Self-organization of blends of a triblock semiconducting copolymer with its component homopolymer represents a novel general approach to preparing organic semiconductor quantum boxes, yielding a large number of quantum boxes having extremely uniform cross-sectional area (ca. 10^{19} boxes/cm^3). Observation of the discrete quantum box states in photoluminescence excitation spectra at room temperature and the remarkable stability of the quasi zero-dimensional excitons with temperature and electric field suggest that the optoelectronic and optical properties of these semiconducting polymer quantum boxes may be significantly enhanced compared to the bulk materials. Electronic localization phenomena and quantum confinement effects in molecular materials that are demonstrated here have also been of long theoretical interest as key elements in the design and construction of molecular switches and molecular electronic devices (9,10,23).

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19. Experimental details. The film thickness of the samples was typically 100 nm and was measured by an Alpha Step Profilometer (Tencor Instruments) which has a resolution of 1 nm. Photoluminescence (PL) and electric field-induced PL quenching measurements were done by using a Spex Fluorolog-2 Spectrofluorimeter. Thin films were positioned such that the emission was detected at 22.5° from the incident radiation beam. For PL measurement under an external field, aluminum was evaporated onto thin film samples on indium-tin-oxide (ITO) coated glass. A positive bias voltage was applied to the ITO electrode, creating an electric field across the film sandwiched between ITO and aluminum electrodes. The samples were illuminated through the ITO-glass side and the PL spectra collected under applied field. Time-resolved (ps) PL decay measurement were performed by using time-correlated single photon counting technique described elsewhere (J.A. Osaheni and S.A. Jenekhe, *J. Am. Chem. Soc.* **117**, 7389 (1995)). Low temperature PL experiments at 77K were done with a liquid N_2 cryostat.

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FIGURE CAPTIONS

Fig. 1. Self-assembling approach to organic semiconductor quantum boxes. (a) chemical structures of the semiconducting polymers from which quantum boxes are made. The difference in π-π* optical gap between PBZT and 2,5-PBO, ΔE_g = 0.81eV, creates a PBZT quantum box in a symmetric 2,5-PBO-PBZT-2,5-PBO triblock copolymer (TBA-1) chain. (b) Microphase separation of the triblock copolymer creates microdomains or boxes of PBZT which are too large to permit observation of quantum confinement effects. (c) self-organization of blends of the triblock with 2,5-PBO homopolymer creates heterostructures in which isolated, ultrasmall, and uniform-sized quantum boxes of PBZT are formed, facilitating observation of quantum confinement effects in optical experiments.

Fig. 2. Optical absorption spectra of thin films of the triblock/homopolymer (TBA-1/2,5-PBO) blend system. Variation with blend composition expressed as mol% PBZT repeat units is shown.

Fig. 3. Photoluminescence (PL) emission spectroscopy of thin films of the TBA-1/2,5-PBO blend system at 298K. (a) PL emission spectra (340 nm excitation) as a function of blend composition. The PL spectrum of PBZT is for 440 nm excitation. (b) A plot of the relative PL quantum efficiency as a function of blend composition for the spectra in (a).
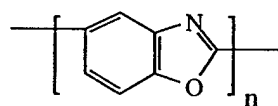
Fig. 4. Room temperature (298K) PL excitation spectra of thin films of the triblock/2,5-PBO blends. The emission was monitored at 600 nm and the PLE spectra were normalized at 470 nm. Arrows mark the new optical transitions that arise in 3-D confined PBZT quantum boxes.

Fig. 5. Temperature and electric field stability of excitons in semiconducting polymers and quantum boxes. (a) Thin film PL spectra (360 nm excitation) of 15% TBA-1/2,5-PBO blend at 298 and 77K, normalized at 580 nm. (b) Thin Film PL spectra (360 nm excitation) of 0.5% blend at 298 and 77K, normalized at 470 nm. (c) Electric field-induced PL quenching of thin films of 2,6-PBO (1), PBZT (2), TBA-1 (3), 12% blend (4), 6% blend (5), 3% blend (6), 1% blend (7) and 0.5% blend (8) sandwiched between indium-tin-oxide (ITO) and aluminum electrodes. The electric field was established by applying a positive bias to the ITO electrode. Illumination was through the ITO-glass and PL emission was detected at 22.5° from the incident light beam. All samples were excited at 430 nm except 2,6-PBO which was excited at 380 nm.
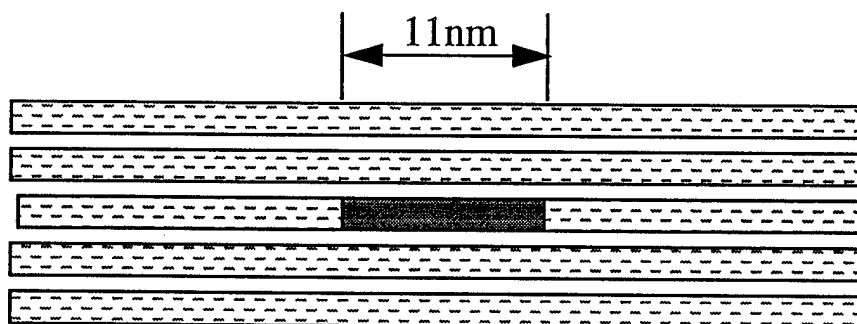
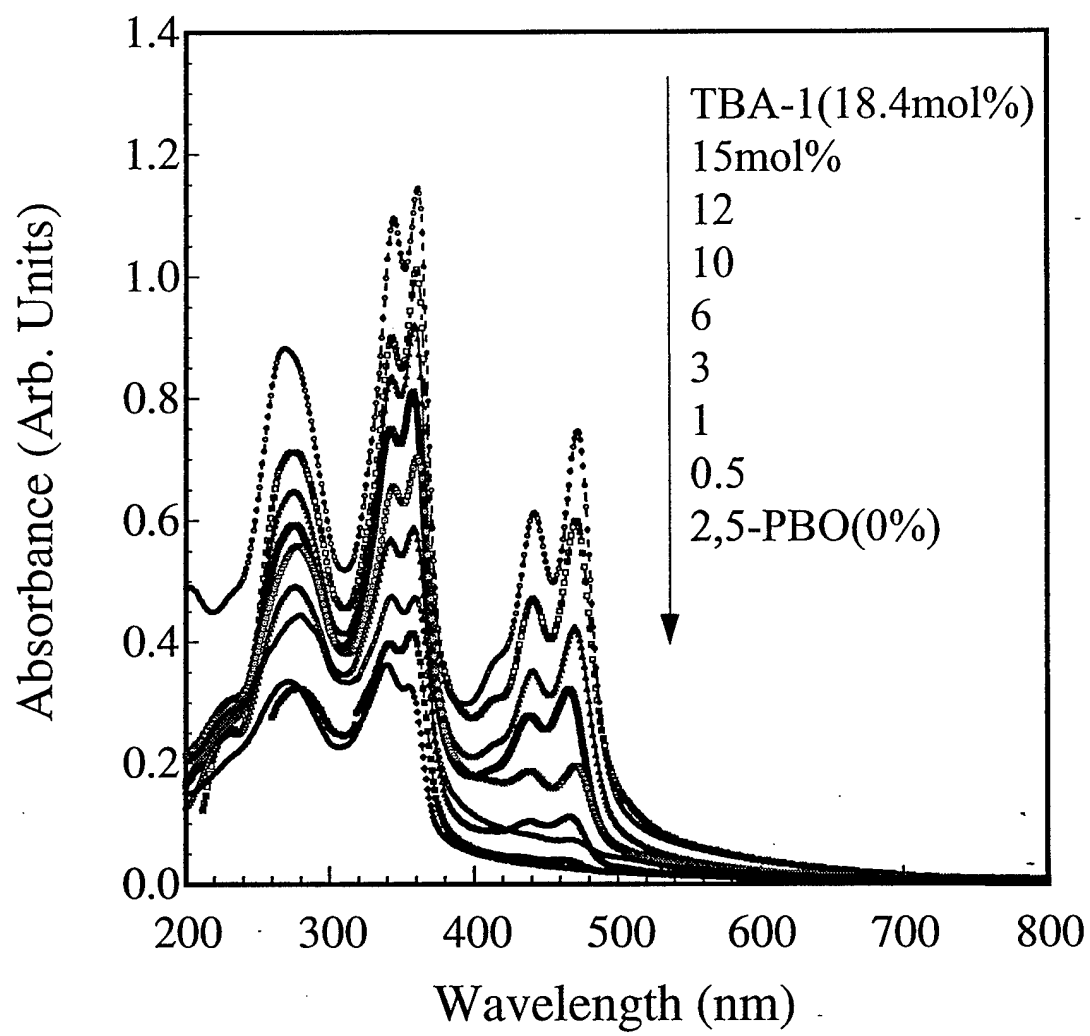Fig. 1

PBZT   2, 5-PBO

a.

TBA-1

b.

23nm   11nm   23nm

A_n B_m A_n

c.

11nm

Fig. 2

Fig. 3

Fig. 4

Fig. 5